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COLD BONDING PROCESS FOR MAKING IRON ORE PELLETS - I

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by

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ABSTRACT

An investigation of the bonding of Canadian iron ore concentrate fines by mixing it with calcium hydroxide in the pelletizing process and by subsequent hardening by exposure to carbon dioxide at room temperature is reported. The maximum crushing strength of pellets produced by this process using only iron ore fines and calcium hydroxide is below the ISO requirement. However, the strength can be increased by the incorporation of a hard material in the pellets. The use of a relatively coarse form of iron ore such as the sinter mix along with the fines is expected to provide the required strength improvement. Significant cost savings are possible in the iron ore pelletizing process by the cold bonding technique.

Keywords: iron ore agglomeration, iron ore pellets, cold bonding by calcium carbonate.

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PROCEDE D'AGGLUTINATION A FROID POUR FORMER DES GRANULES DE MINERAI DE FER - I

par

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RESUME

Le présent rapport expose une étude sur l'agglutination des fines de concentrés de minerai de fer canadien en les mélangeant avec de l'hydroxyde de calcium durant le processus de granulation et en les laissant par la suite durcir à la température ambiante par exposition au bioxyde de carbone. La résistance maximale au concassage des granules produites à l'aide de ce procédé, selon lequel on utilise seulement des fines de minerai de fer et de l'hydroxide de calcium, est inférieure aux normes de l'ISO. Cependant, la résistance peut être accrue en incorporant une matière dure dans les granules. On prévoit que l'utilisation d'une fame de minerai relativement grossier tel que le mélange fritté avec les fines permettra une augmentation nécessaire de la résistance. Grâce à la technique d'agglutination à froid, il est possible de réaliser des économies importantes dans le procédé de granulation du minerai de fer.

Mots-clés: agglomération du minerai de fer, granules de minerai de fer, agglutination à froid au moyen du carbonate de calcium.

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COLD BONDING PROCESS FOR MAKING IRON ORE PELLETS - I

The agglomeration of iron ore fines and concentrates using the pelletizing process and subsequent induration procedures has been in use by the iron ore industry in North America for at least the last thirty years (1,2,3). Traditionally, bentonite is used as a binder for the agglomeration process. This binder meets the general requirements for good quality pellets, viz., sufficient strength for handling in the green and dry states, sufficient induration strength for storage and transportation and also excellent reducibility in iron making furnaces without disintegration. However, bentonite can affect the quality of the product because of the increase in the silica and alumina content in the system. Moreover, good quality bentonites are being gradually depleted. Because of these reasons, during the past few years, there has been an increasing interest shown by the iron ore producers to look for an alternative binder or binders to replace bentonite. Among the various binders investigated, several organic polymers and peat moss have shown substantial promise (4,5,6).

The bonding of iron ore concentrates at low ambient temperatures (without a high temperature induration step) is known as the cold bond pelletizing process. This process is still at a very early stage of development (7,8,9). The advantages of a cold bonding process are tremendous - the elimination of the induration step at temperatures of 1300°C will effect substantial reductions in the cost of production of iron ore pellets through reduced energy consumption, and capital and maintenance expenditures on high temperature furnaces. Three types of cold bonding processes have been reported in the literature (3) for iron ore pellets. They are:

1. The Grangcold process using portland cement as a binder;
2. The COBO and MTU cold-bond processes using lime and silica as the principal ingredients which form calcium silicate bonds under hydrothermal conditions; and
3. The carbonate bonding process which forms calcium carbonate bonds resulting from the reaction between alcium hydroxide and carbon dioxide.

Originally, the carbonate bonding process was developed for the agglomeration of steel-plant byproducts. Subsequently, Imperato (9) of the Blocked Iron Ore Corporation, New York, applied this technique for pelletizing iron ore concentrates. Good physical and chemical properties of the carbonate-bonded pellets were reported and these pellets also performed satisfactorily in the blast furnace. Since then there have been several studies on this process (3,7) but the information available in the literature is insufficient for the manufacture of carbonate bonded pellets, especially for Canadian iron ore concentrates. This report deals with the results of an investigation carried out at CANMET on the cold bonding of Canadian iron ore concentrate fines by the carbonate technique.

In the carbonate bonding process, the hardening of the pellets occurs through the reaction between calcium hydroxide and carbon dioxide to form calcium carbonate ($CaCO_3$) and/or calcium basic carbonate ($CaCO_3.Ca(OH)_2$) bonds which have considerable mechanical strength. The process may be represented by the following chemical equations:

$$Ca(OH)_2 + CO_2 \text{ ------> } CaCO_3 + H_2O$$

$$2Ca(OH)_2 + CO_2 \text{ ------> } CaCO3.Ca(OH)_2 + H_2O$$

However, the strength of the resultant pellets is closely related to several processing parameters such as the lime content, moisture content, particle size of the ore and the extent of carbonation.

EXPERIMENTAL

Materials

Iron Ore Concentrate

The iron ore concentrate used for the experimental work was obtained from the Carol Lake processing plant of the Iron Ore Company of Canada. It consisted principally of specular hematite and varying amounts of magnetite. It also contained small amounts of quartz and feldspar. Typical chemical composition of the iron ore concentrate used is given in Table 1.

Calcium Hydroxide

Fisher certified reagent grade calcium hydroxide was used for the experiments.

Procedure

The calcium hydroxide was mixed with the iron ore concentrate in a Turbula mixer*. Normally a 2 kg batch of the concentrate was used and the amount of calcium hydroxide was varied in order to study the effect of bond concentration. In a few cases, quantities of sand or coke were also added to the ingredients for determining the influence of such additions on the strength of the pellets.

Pellet Preparation

Spherical pellets were prepared from the mix by the balling technique using a rotating tire pelletizer. Seed pellets were initially made and were then used to enhance pellet growth by the continuous addition of dry mix and water to the system until the desired pellet size was obtained. The final pellets were -12.5 mm + 11.2 mm (-1/2" + 7/16") in size.

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* Manufactured by W.A. Bachofen, Switzerland

Testing

The as prepared pellets were characterized by the drop test and wet compressive strength. The dry compressive strength was determined after drying the pellets at 125°C in an air oven.

Carbonator

Three types of carbonator vessels were used for the pellet carbonation process. They were:

(i) Pressure carbonator. In this case the pellets were kept inside a closed metal container fitted with a pressure gauge and carbon dioxide inlet and the carbonation reaction was carried out under a constant pressure of about 70 KPa (10 psig).

(ii) Open glass vessel. In this procedure, the pellets were placed inside a beaker with a partially open cover. The carbon dioxide was fed to the bottom layer of the pellets using a glass tube. A continuous flow of carbon dioxide was maintained to the system during the carbonation process.

(iii) Tower reactor. In this process the pellets were placed in a cylindrical glass tower 2.5 cm in diameter x 15 cm in length, and carbon dioxide was continuously fed from the top to the bottom through the pellet bed. The difference between (ii) and (iii) was that in (iii) a more uniform flow of carbon dioxide through the pellet bed was obtained and the water produced in the carbonation reaction was automatically drained from the tower.

RESULTS AND DISCUSSION

The Effect of Different Carbonators

A batch of iron ore pellets using 12% by weight calcium hydroxide in the mix was prepared and samples of these were carbonated using the three types of carbonators described above, for various periods of time. The pellets for these tests were dried at 99°C for about 30 minutes. The pressure reactor (i) produced pellets with a crush strength of only about 30N. This

was because the water formed in the reaction between calcium hydroxide and carbon dioxide could not escape from the system and remained in the pellets. Reactor (ii) produced pellets with a crush strength of about 200N, much better than the pressure reactor, but was still not satisfactory because part of the water formed in the reaction flowed down the sides of the vessel and was re-absorbed by the pellets. In the tower reactor (iii) however, most of the water formed was drained through the gas exit port which resulted in little or no moisture re-absorption by the pellets giving a crush strength of about 300N. Hence, the tower rector was selected for further carbonation studies.

In Table 2 are listed the amounts of calcium hydroxide used in the various batches of the pellets made, the drop number and the green (wet) and dry compressive strengths measured on the products. The drop number of 3 to 4 of the pellet mixes is almost independent of the calcium hydroxide concentration; the green strength and dry strength are both lowest at the lowest 8%) calcium hydroxide content, but are similar at 10 and 12 wt %. The incorporation of sand or coke particles with the lime in the pellets does not seem to have any significant effect at this stage.

The Effect of Pre-Carbonation Moisture Content of the Pellets on Carbonated Pellet Strength

Initial experiments on the carbonation-hardening of the pellets showed that the wet green pellets did not develop any appreciable strength on carbonation. The green pellets were therefore dried to various levels of moisture content before carbonation by heating in an air oven at 99°C for various time intervals. The effect of moisture content of the pellets on carbonation-hardening was then evaluated. The weight loss of the samples at the respective time intervals was used to estimate the moisture content at each level, knowing the original water content of the green pellets (about 10 wt %). The partially dried pellets were then subjected to carbonation for different

periods of time in the tower reactor and the strength of the resulting pellets was measured by the standard crushing tests. The various drying and carbonation times, the moisture content of the partially dried pellets and the compressive strengths measured on these different specimens are recorded in Table 3.

A short drying time of 10 minutes at 99°C produces pellets with a high moisture content of about 9% and on carbonation for 30 min. they show a crush strength of less than 40N. Also, an increase of carbonation time does not influence this low strength significantly. By increasing the drying time of the green pellets from 10 to 40 min. at the same drying temperature, the moisture content of the pellets drops to about 6% and the product-strength increases to about 300N on carbonation for 30 min. Here again, extended carbonation time to about 240 min. does not have an appreciable effect. However, when the pellets are dried further to a moisture content of about 3% in the 24 hour drying cycle, the pellet strength again drops to about 60N after carbonation for 60 min. These observations indicate that the moisture content of the pellets before carbonation has to be within a specific range for strength development on carbonation. The reason for this behaviour is believed to be the differences in the chemical reactions that are possible under different water contents. For example, when the water content is high, the reaction between calcium hydroxide and carbon dioxide can produce calcium bicarbonate according to the equation:

$$Ca(OH)_2 + 2\ CO_2 \text{ -----> } Ca(HCO_3)_2$$

Under limited availability of water, however, the reaction would be the formation of calcium carbonate:

$$Ca(OH)_2 + CO_2 \text{ -----> } CaCO_3 + H_2O$$

Calcium bicarbonate is soluble in water while calcium carbonate is insoluble so that when excess water is present, the strength

development does not occur with the carbonation of calcium hydroxide. A moisture content of about 6% appears to be an optimum for strength development.

The Effect of Calcium Hydroxide Content on the Strength of Carbonated Pellets

In Table 4 are listed the results of the carbonation experiments on pellets made from various compositions after drying them for 40 min. at 99°C, to a water content of about 6%. Experiments 1 - 3 show the effect of calcium hydroxide concentration on the strength of pellets after carbonation for 4 h. At the 8% level of calcium hydroxide the strength is quite low at 20N. At 10% calcium hydroxide, the strength increases to about 300N and at 12%, to about 400N. Increased calcium hydroxide content in the mixture thus increases the final carbonated strength of the pellets, although not proportionately. Experiments 3 - 6 show the general reproducibility of the technique at 12% calcium hydroxide concentration - the strength varies between 370 and 430N.

The last four experiments in Table 4 illustrate the effect of adding coarse sand or coke to the mix on the strength of carbonated pellets under extended carbonation (24 h) conditions. Pellets made with only 12% by weight of calcium hydroxide develop a crush strength of about 540N in 24 h. The addition of 30% sand in either mesh size increases the carbonated crush strength to 950-980N in 24 h. The addition of 10% by weight of -30+50 μm mesh coke does not show any increase in strength although the volume fractions of the two additives are comparable. This shows that the incorporation of a strong hard material in a coarse form improves the compressive strength of the hardened pellets - sand is stronger and harder than coke. This effect may be likened to the effect of incorporating aggregates (crushed stone) into portland cement to make concrete of increased compressive strength. The addition of the coarse material serves two purposes - one, it reduces the amount of material to be

carbonated in the same volume and also increases the total porosity thereby providing a faster hardening time; two, the admixture of a strong hard material with the powder increases the overall compressive strength of the pellets. Incorporation of coarse particles of iron ore with the iron ore fines, thus, appears to be a possible way of increasing the strength of the cold bonded iron ore pellets.

The Action of Heat on Carbonated Pellets

Differential thermal analysis (DTA) was used to determine the thermochemical behaviour of the carbonated pellets. The three DTA curves, A, B and C, in Fig. 1 represent respectively, pellets made without any calcium hydroxide, pellets made with 12% calcium hydroxide carbonated for 4 h, and pellets with 12% calcium hydroxide carbonated for 8 h. All the curves show an exothermic peak at about 300°C, and endothermic peaks at about 850°C. However, curves B and C show an endothermic peak at about 500°C also, which is absent in curve A. The exothermic peak at 300°C is presumably due to the oxidation of the manganese minerals that are present in the original iron ore concentrate and is common to all three samples. The endothermic peak at about 500°C represents the dehydration of calcium hydroxide and the endothermic peak about 850°C corresponds to the decomposition of calcium carbonate. The presence of calcium hydroxide in samples B and C indicates that the carbonation is incomplete even after 8 h in pure carbon dioxide. The carbonate decomposition peak at about 850°C is considerably larger after carbonation for 8 h as expected because of the greater degree of carbonation at the longer time interval. The small amount of calcium carbonate that is present in the original iron ore yields a small endothermic peak for the sample without any added calcium hydroxide.

Figure 2 represents the DTA curve of the carbonated pellet after a carbonation time of 72 h. The endothermic peak at about 500°C has disappeared in this case showing that all the calcium

hydroxide has reacted after 72 h in flowing carbon dioxide.

Microstructural Features of the Carbonated Pellets

The microstructure of the cold bonded pellets was investigated by examining the fracture surfaces of the pellets. Figure 3 is a scanning electron micrograph of a partially oven-dried pellet before carbonation. The material consists principally of platy to lath-shaped specular hematite together with finer grains of iron oxide and calcium compounds (hydroxide and carbonate). Figures 4, 5 and 6 show the SEM micrographs of the pellets after carbonation for 1, 24 and 72 h respectively. Because of the poorly developed anhedral nature of the calcium carbonate that is formed, the difference between the various samples is not clearly visible; the grain size of the calcium carbonate appears to vary from sample to sample. At a higher magnification, however, the growth of anhedral carbonate grains both in a randomly oriented fashion and epitaxially on the basal plane of the specular hematite is discernible (Fig. 7).

CONCLUSIONS

Iron ore concentrate fines (-44 μm) pelletized with calcium hydroxide and water harden when exposed to carbon dioxide gas. The strength of the hardened pellets is a strong function of the amount of calcium hydroxide used and also of the water present in the pellets before carbonation. With 12 wt % calcium hydroxide in the mixture, a water content of about 6 wt % appears to be satisfactory for the carbonation reaction, and this level of moisture can be obtained by the partial drying of the green pellets.

The strength of the carbonated pellets made from iron ore concentrate fines along with 12% calcium hydroxide is only about 740N which is far below the 2000N required in the ISO specifications. However, the inclusion of a hard material in a relatively coarse form increases the compressive strength of the pellets on carbonation. In the present investigation, sand,

which is not acceptable in iron ore pellets, was used as an experimental strong coarse material. A combination of a coarse form of iron ore, such as sinter feed, and fine concentrate together with calcium hydroxide in the right proportions, is expected to provide a process for fabricating sufficiently strong pellets by the cold-bonding technique. Some of the advantages of such a process over conventional methods are:

(1) bentonite is not required for the process,
(2) the process is carried out at near room temperature so that the high temperature sintering step can be avoided, and
(3) self fluxed pellets also may be fabricated.

ACKNOWLEDGEMENTS

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Table 1. Composition of the Carol Lake Iron Ore Concentrate

Analysis	Wt %
Total Fe	64.8
SiO_2	4.8
Fe_3O_4	36.8

Table 2. Mix Composition, Drop number, and Green and Dry Strength of Pellets.

Mix No.	$Ca(OH)_2$ wt%	Drop No. X	Strength, N	
			Green	Dry
1	8	3.3	8.5	20
2	10	4.0	15.0	70
3	12	3.5	17.0	23
4	12	3.0	16.0	40
5	12	3.0	13.0	60
6	12	3.0	16.0	60
7	12*	5.0	26.0	80
8	12#	5.0	27.0	60
9	12+	6.5	17.0	70

* with 30 wt % sand -16 to +30 mesh
# with 30 wt % sand -30 to +50 mesh
+ with 10 wt % coke -30 to +50 mesh

Table 3. The Effect of Drying Time and Moisture Content on the Strength Development of Pellets on Carbonation.

Calcium Hydroxide = 12 wt %

Drying Time, min	Moisture Content %	Strength (N) at Carbonation Time, min 30	60	120	240
10	9.15	40	32	30	30
20	7.52	40	50	48	92
30	6.02	190	260	190	296
40	5.66	300	270	316	310
1440	3.00	-	60	-	-

Table 4. Data on the Strength Development of Pellets of Varying Compositions on Carbonation.

Expt. No. (Mix No.)	% $Ca(OH)_2$	Strength (N) at Carbonation Time, h 0.5	1.0	2.0	3.0	4.0	24.0
1	8		-	20	-	20	-
2	10	260	210	293	222	300	-
3	12	40	-	-	-	430	-
4	12	410	540	470	450	400	-
5	12	280	290	360	400	370	-
6	12	310	-	-	-	-	540
7*	12	440	-	440	450	480	950
8#	12	310	-	370	-	390	982
9+	12		60	-	-	184	404

* with 30 wt % sand -16 to +30 mesh
\# with 30 wt % sand -30 to +50 mesh
\+ with 10 wt % coke -30 to +50 mesh

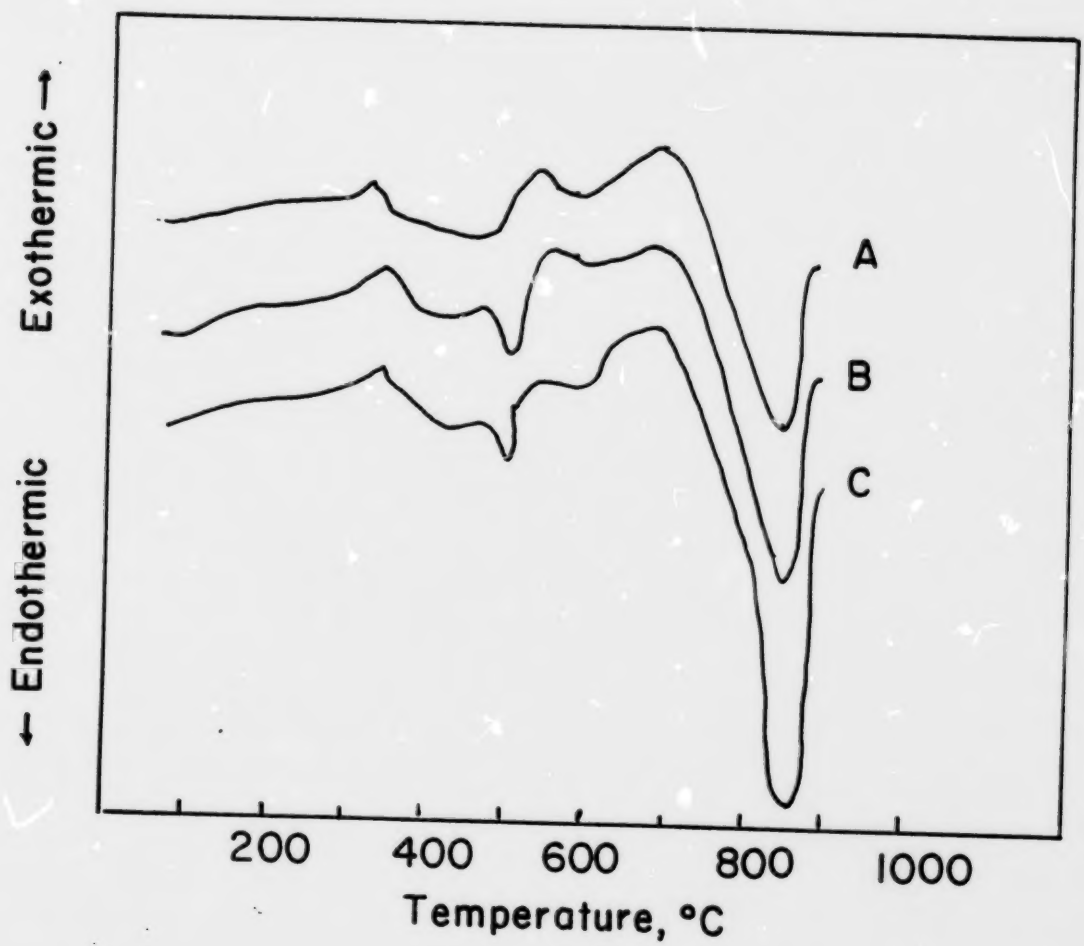

Fig. 1. DTA curves for pellets - (A) pellet without carbonation, (B) pellet subjected to 4 h carbonation and (C) pellet subjected to 8 h carbonation.

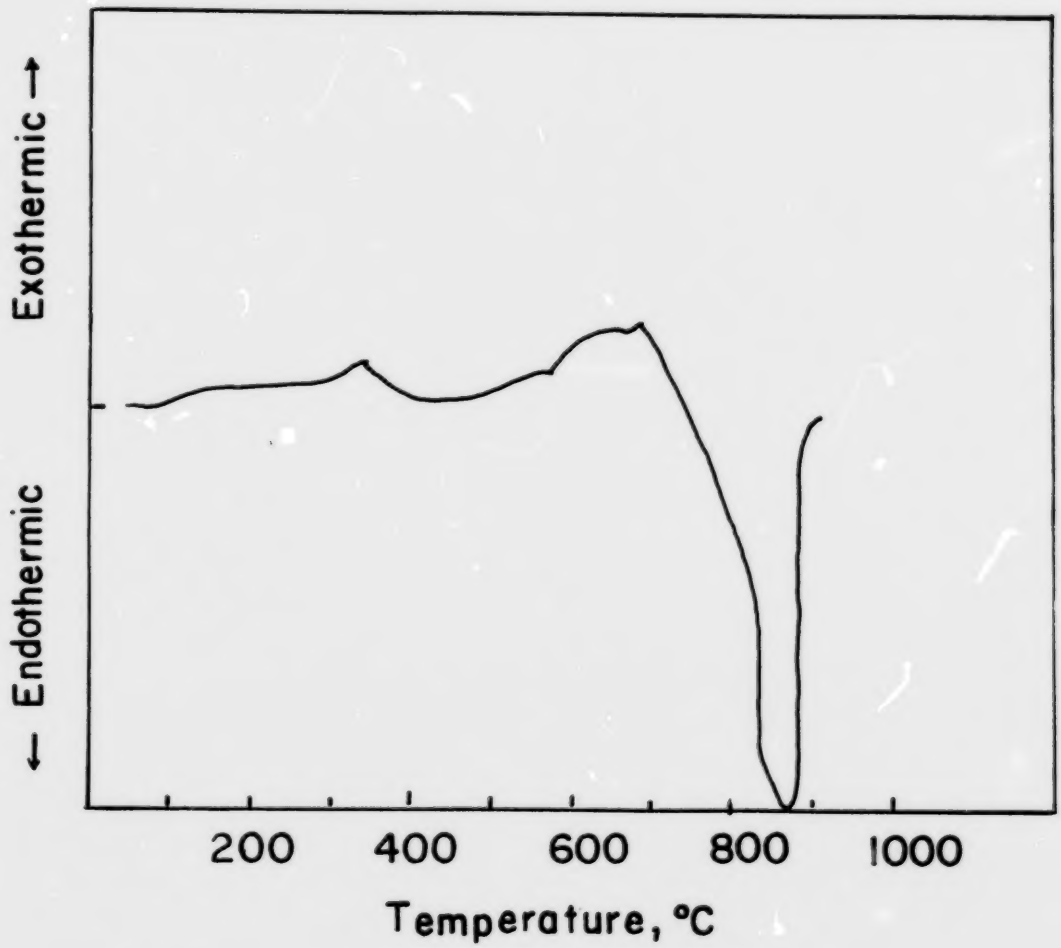

Fig. 2. DTA curve showing complete conversion of calcium hydroxide to calcium carbonate for pellet subjected to 72 h carbonation.

Fig. 3. SEM micrograph of fracture surface of oven dried pellet.

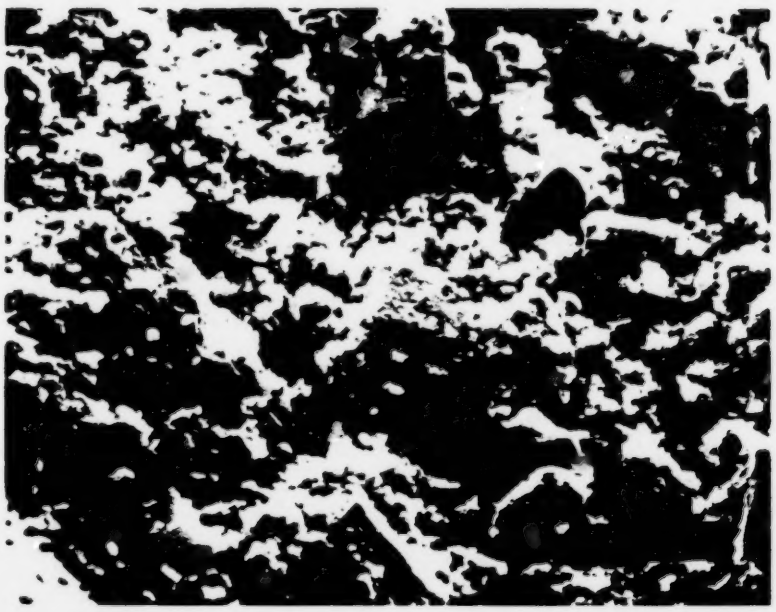

Fig. 4. SEM micrograph showing the morphology of pellet after 1 h carbonation.

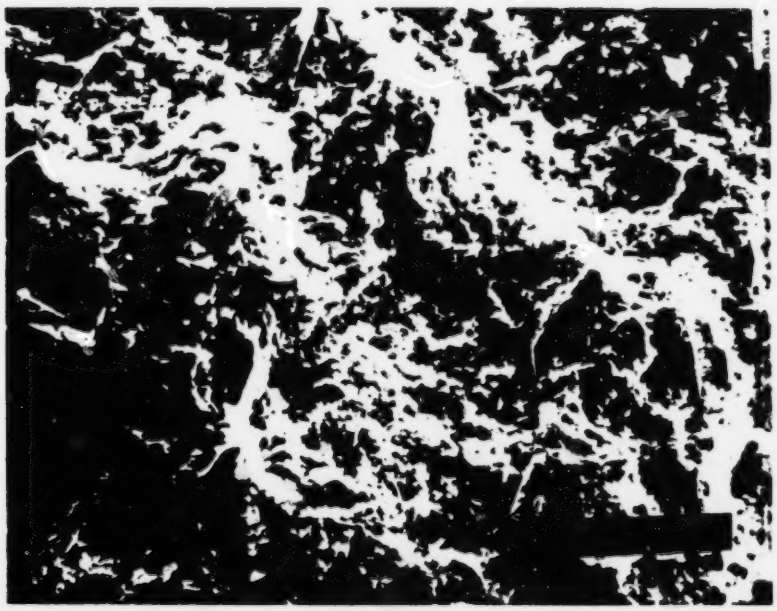

Fig. 5. SEM micrograph showing the morphology of pellet after 24 h of carbonation.

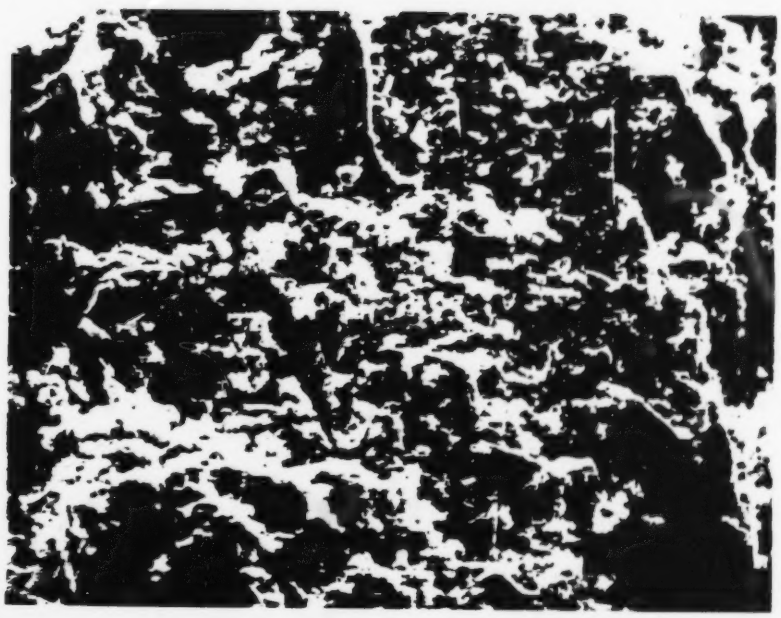

Fig. 6. SEM micrograph showing the morphology of a pellet after 72 h of carbonation time.

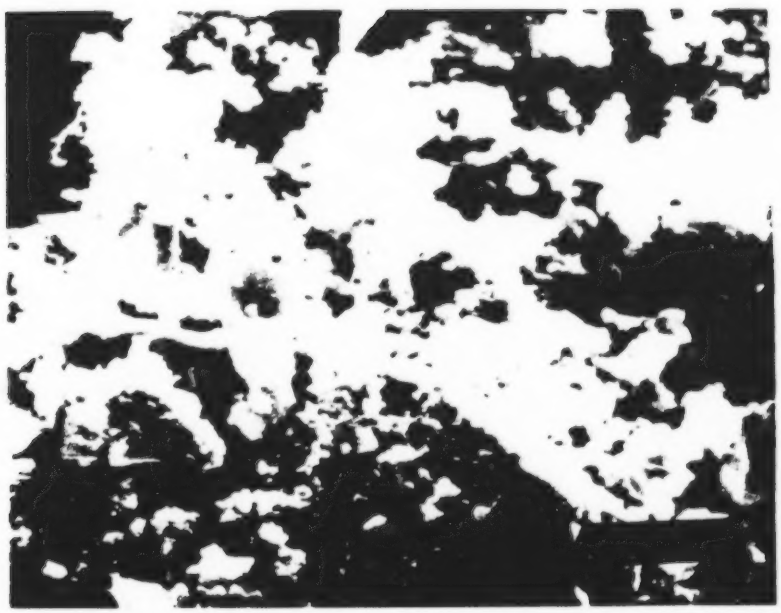

Fig. 7. SEM micrograph showing development crystallites of calcium carbonate grown epitaxially on iron oxide platelets.